TRACE CHEMICAL MINE DETECTION DATA COLLECTION

FINAL SCIENTIFIC AND TECHNICAL REPORT

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CONTRACT NUMBER:	**DAAB15-01-C-0017**
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List of abbreviations:

CECOM	US Army Communications-Electronics Command
NVESD	Night Vision & Electronic Sensors Directorate
MEDDS	MECHEM Explosives and Drug Detection System
UXO	Unexploded Ordnance
DCMA	Defense Contract Management Agency

1 SCOPE

This final scientific and technical report outlines the progress made during Phases 1 and 2 of the trace chemical mine detection comparative testing using the MECHEM MEDDS and NOMADICS FIDO systems at Rakovo Polje Test Site in Croatia from July 2001 to August 2003 and summarizes the conclusions and recommendations from the test results obtained.

A Final Meeting at the Doubletree Hotel at Falls Church/Tysons Corner in Virginia, USA was held from Monday, 4 August to Wednesday, 6 August 2003. Representatives from MECHEM, NOMADICS, CROMAC, CSIR (Defencetek) as well as NVESD attended the meeting. The purpose of this meeting was to use the information gathered during the project to draw up a final technical and scientific report as conclusion of the project. This report also reflects the views expressed at that meeting taking into account the results of the sampling as well as other related criteria.

2 APPLICABLE DOCUMENTS

The following documents form part of this report to the extent mentioned herein:

2.1 Proposed Contract for Trace Chemical Mine Detection Data Collection. Ref. AMSEL-AC-WB-B issued by US Army CECOM Acquisition Center, Washington on 10 July 2001.
2.2 Minutes of First Project Meeting conducted at UNMAAP Conference Center in Zagreb on 16 July 2001.
2.3 Minutes of Second Project Meeting conducted at Hotel Niko in Diklo on 18 July 2001
2.4 Test Plan for Trace Chemical Mine Detection Data Collection issued by MECHEM on 23 August 2001.
2.5 Progress Report No1 – Site Selection and Establishment. Document issued by MECHEM on 27 September 2001.
2.6 Progress Report No 2 – Results of Vapour Sampling conducted from 10 to 13 September 2001.
2.7 Progress Report No 3 – Results of Vapour Sampling conducted from 6 to 10 November 2001.
2.8 Progress Report No 4 – Vapour Sampling 6 –10 November 2001: NOMADICS Results.
2.9 Progress Report No 5 – Postponement of Vapour Sampling planned for 14-26 April 2002.
2.10 Progress Report No 6 – Postponement of Vapour Sampling planned for 3-8 June 2002.
2.11 Progress Report No 7 – Results of Vapour Sampling conducted from 15 to 19 July 2002.
2.12 Progress Report No 8 – Vapour Sampling 15 – 19 July 2002: NOMADICS Results.
2.13 Proposal Modification: Statement of Work DAAB 15-01-R1017 dated July 2002.
2.14 Amendment of Solicitation/Modification of Contract issued by USA CECOM Acquisition Ctr-Washington, dated 23 Sep 02.
2.15 Minutes of a Project Meeting held at the MECHEM Office in Velika Gorica at 09:00 on 23 Sep 02.

2.16 Minutes of a Project Meeting (Meeting no 2) held at the MECHEM Office in Velika Gorica at 11:00 on 26 Sep 02.
2.17 Minutes of a Project Meeting (Meeting no 3) held at the MECHEM Office in Velika Gorica at 13:00 on 27 Sep 02.
2.18 Minutes of a Special Meeting held between MECHEM and NOMADICS on the Design of the Vapour Sampling Filter held at the MECHEM House in Velika Gorica at 12:00 on 28 Sep 02.
2.19 Minutes of a Special Meeting held between MECHEM and NOMADICS on the Design of the Vapour Sampling Filter held at NOMADICS, Stillwater, Oklahoma, USA, at 15:00 on 23 Oct 02.
2.20 Report 10: Report on the Workshop held at NOMADICS Inc, Stillwater, USA, from 21 to 23 Oct 02 dated 22 Nov 02.
2.21 Report 11: Interim Report on the Filter Tube Design dated 8 Jan 03.
2.22 Minutes of the planning meetings held between MECHEM and NOMADICS on the design of the vapour sampling filter tube held at MECHEM, Pretoria, South Africa, from 13 to 18 February 2003.
2.23 Progress Report 12: Vapour Sampling 31 March to 5 April 2003.
2.24 Progress Report 13: Final Report on the Filter Tube Enhancement.
2.25 Progress Report 14: Vapour Sampling 26 to 30 May 2003.

3 INTRODUCTION

During demining operations, areas suspected of containing mines are often found to be free of mines. If there were a method for determining if an area was free of mines, resources could be refocused to areas that are known to contain mines, leading to a great reduction in demining costs and time wasted demining areas that were already free of mines. The MEDDS system (See Appendix A for detail) was designed to specifically address this problem. It was designed and recognized to be an area reduction system, whereby areas containing traces of explosive vapor could be distinguished from areas containing no such explosive traces. The utility of this system is that only those areas identified to contain explosive traces have to be manually demined/searched for the explosive source – and the areas where no such sources are identified could be declared safe and need not be demined.

It had been demonstrated prior to these tests that traces of explosives escaping from mines do not necessarily remain localized directly over the mine, but can be dispersed meters from the source by environmental factors. Furthermore, the spread of contamination is not necessarily uniform in all directions, nor is it always greatest directly over a mine. Because of these factors, it was clear that the MEDDS system was not suitable for detecting the exact position of any individual mine. Rather, the system is useful for determining whether or not an area contains mines. This is an important distinction that must be kept in mind when interpreting the results of these tests.

The MEDDS system, and several adaptations of the system known by different names, has been internationally recognized as an explosive vapor detection system. There have been a number of papers written and published about the system. These papers can be referenced as background information on the system.

As further background it should be explained that landmines and unexploded ordnance (UXO) produce a vapor signature that often contains traces of the explosive (i.e., TNT or RDX) contained in the device. These explosives are not chemically pure, which gives rise to other vapors (2,4-DNT and others), derived from the parent explosive. Explosives such as TNT also degrade once released into the soil, producing chemicals that are additional sources of vapor that could be detected by dogs or sensitive chemical sensors. These vapors are not naturally occurring, so when they are present in the environment there is a high probability that landmines or UXO are in the area. These devices also give off other vapors originating from the plastic, paint, rubber, and other materials used to construct the device. However, these materials are very common and are not unique to landmines. Hence, a detector capable of detecting vapors emanating from the non-explosive components of a mine could be prone to false positive responses in areas littered with, for example, plastics and rubber. Hence, it is desirable for the detector to sense explosives and explosives-related chemicals.

Together, the vapors originating from a mine form a scent that is specific to each type of UXO or landmine. This signature occurs in the field as a vapor plume or trail of vapors absorbed onto the vegetation, soil and other surfaces. If a detector is able to detect the explosive vapor or vapor-contaminated particulates, or a combination of both, then it will be able to locate areas contaminated with mines, even if other vapors such as those given off by plastics and paint are also present in the area.

One of the most effective means of mine detection today capitalizes on the highly specific and highly sensitive olfactory capabilities of canines. In the demining community, there is a general acceptance that a set of trained dogs is an extremely effective means of detecting mines. These dogs can be trained to carry out one of two different mine detection tasks:

- The detection of chemicals such as the explosives RDX or TNT. Such dogs are referred to as “Chemically Specific Dogs”.

- The detection of the mixture of smells/odours including the plastic, rubber, etc. that makes up the smell of the complete explosive device. Such dogs are referred to as “Bouquet Dogs”.

The MEDDS system uses chemical dogs to analyze samples off-site. MECHEM’s present approach is to train in-country personnel to collect vapor samples, which are then screened at a climatically controlled dog analysis center using chemically specific dogs to do the detection. Presently MEDDS, or as it is also referred to as REST (Remote Explosive Scent Tracing), is accepted by the United Nations as a demining method.

What is important to note is that negative results showing that **no explosives are present** is accepted as an indication that an **area** is free of mines. Positive tests are followed up with additional clearance techniques to pinpoint the exact location of the explosive source and back up the result. Simply put, MEDDS should not be considered as a demining method but rather as a system for eliminating sectors that do not contain traces of explosives or target scent. It is thus an area reduction system and not a specific mine position detector.

An aspect of the current proven MEDDS technology is the reality that samples usually have to be analyzed off-site. Samples are collected and transported to a test facility usually remote from the collection area. Use of a remote test facility makes it possible for the canines to analyze samples in a controlled environment in which the scent background does not change appreciably from day to day. In addition, the dogs always work in a comfortable environment. This greatly reduces fatigue of the dog and handler, making it possible to analyze more filters per day. However, transport of the samples to a remote facility delays analysis of the sample. Clearly, a means for testing the samples immediately after sampling or at least without a long delay would mean that the same teams could be used for the initial sampling and for the follow-up investigation of a suspect area if a sample is found to be positive.

One possible method for on-site analysis of MEDDS-type samples is to utilize sensitive electronic sensors to detect explosives in the samples. Nomadics, Incorporated of Stillwater, Oklahoma has developed a sensor to detect the presence of explosives based on sensing their unique chemical vapor signature. Nomadics Fido detection system uses a breakthrough technology developed at the Massachusetts Institute of Technology (MIT) by Professor Timothy Swager. Amplifying fluorescent polymer (AFP) technology allows the detection of TNT and related substances at levels three orders of magnitude below that of the most sensitive commercially available laboratory instruments, making it possible to detect the extremely low concentrations of explosive vapors encountered in the vicinity of landmines. During limited side-by-side field-testing of the FIDO sensor with canines at Fort Leonard Wood, Missouri, the FIDO sensor was able to detect landmines at performance levels similar to that of trained canines. To date, the FIDO sensor is the only trace chemical vapor sensor that has demonstrated this ability in field tests.

Additional technical information regarding the FIDO sensor is included in Appendix B.

4 PURPOSE

The purpose of contract DAAB15-01-C-0017 signed on 10 July 2001 (See Ref 2.1) was to perform comparative testing in Croatia between the MECHEM MEDDS and the Nomadics Fido systems respectively in order to demonstrate the relative abilities of the two systems to detect the presence of landmines as well as determine areas that are clear of land mines. In addition the scope of the contract required the performance of MEDDS in general to be compared to the performance of the Fido vapor and particle detection systems.

The ultimate objectives were to determine whether the existing MEDDS technology could be enhanced or augmented by the incorporation of Fido as well as providing information as to the utility of Fido for humanitarian demining.

5 DESIGN, SELECTION AND ESTABLISHMENT OF THE TEST FIELD

5.1 Test Field Design

The design of the test field was the subject of long discussion at the first and the second Project Meetings held on 16 and 18 July 2001 in the UNMAAP Centre in Zagreb and the Hotel Niko in Diclo respectively (see Ref 2.2 and 2.3).

With reference to the purpose and the use of the MEDDS System the main point of debate was whether to create a simulated mine field in a portion of the test field (and then require the MEDDS/Fido systems to locate and identify the mined area) or to randomly deploy an unknown number of landmines throughout the entire test area.

Notwithstanding clear statement of the fact that the latter option would test the system for something that it was not designed to do (i.e., to pinpoint the exact location of landmines in a field), there was pressure towards satisfying a scientific requirement to determine how far from a landmine the system was able to detect traces of explosives, and hence the presence of a mine. This was due to the belief by chemists at the time that vapor would travel no more than 30 meters from the source. A decision was made to create an “area reduction” test field in which 8 to 15 individual landmines were randomly distributed over a 40,000 square meter test field. The number, type, burial depth, and locations of mines in this area were not revealed to MECHEM or Nomadics until after the final sampling was completed and all test results had been submitted to NVESD (in the test field three PROM-1, three TMA-1A, three PMA-2 and three PMA-3 mines buried at 10, 15 and 20cm beneath the surface respectively were planted). The test field and procedure were designed to determine to what extent it was possible to determine the presence and location of the landmines. Each sample would be taken from a lane 4 meters in width and approximately 50 meters in length (approximately 200 square meters of field covered per sample). For each sampling, the area reduction field was sampled twice. One set of samples was collected by sampling rows that ran the length of the field (28 rows of samples with seven samples per row, for a total of 196 samples). The second set was collected by sampling columns that ran the width of the field perpendicular to the lengthwise rows of samples (86 columns with two samples per column, for a total of 172 samples).

In addition, it was decided that a separate test field would be established adjacent to the area reduction field for the purpose of addressing the scientific requirement of determining how far trace levels of contamination could be detected away from a mine. This field, referred to as the “sensitivity” or “proximity” test field, would contain 12 landmines (three PROM-1, three TMA-1A, three PMA-2 and three PMA-3 mines buried at 10, 15 and 20cm beneath the surface respectively) placed at known positions in a grid that would allow 30 meters between these mines. The proximity field would also be separated from the area reduction field by a 30-meter wide lane containing no mines. Samples were to be taken along and up to 2 meters on each side of concentric circles at 3, 7 and 11m from the mine, starting with the 11-meter circle and working inward. The purpose of this test was to monitor the extent of the spreading of explosive vapor (or contamination) from the mine over the duration of the project. The 30-meter spacing between mines was an estimated upper limit to how far contamination would spread from a mine, based mostly on anecdotal evidence from a variety of sources. In retrospect, this spacing was too small based on the outcome of the tests described in this report.

Sampling on the site was initially planned to take place 60 days and 6 months after the placement of the landmines but it was agreed that a sampling immediately after the mines were placed, could possibly also have some scientific value. MECHEM offered to add a third sampling to satisfy this requirement.

The detailed design of the Test Field was reported in the MECHEM Report “Test Plan for Trace Chemical Mine Detection Data Collection” dated 5 September 2001 (See Ref 2.4). This clearly stated the requirements and characteristics of the required test field.

5.2 Test Field Selection

CROMAC was requested to identify four potential sites for the establishment of the test site. The most important requirement for the test site was that it was required to be free from any landmines (in order not to endanger the lives of the personnel required to conduct the tests) and that it should be free from any explosive contamination.

Four sites were identified and the Project Team visited these over the period 16 to 20 July 2001. One of the sites (Varkasic) was rejected due to the presence of extremely heavy vegetation and spot vapor samples were taken at the other sites to verify the absence of explosive contamination. Evidence of a battle zone on one other site (Paljuv), and the possibility of a landmine threat at this site, led to the suspension of efforts to verify the presence of explosive vapor. Upon analysis of filters from the three sites that were sampled, evidence of contamination was found at all sites making them unsuitable for use as a test area. CROMAC was requested to identify one more site and spot vapor samples were taken on a site on the outskirts of Sisak (Rakovo Polje) on 27 Jul 01.

Following the analysis of all the spot vapor samples by MECHEM and NOMADICS it was found that the site at Rakovo Polje was the more suitable and a decision was taken to establish the test field at this location.

Important Note

Neither MECHEM nor Nomadics was able to detect explosives contamination in samples from this site prior to the mines being placed at the site. The fact that the site was found to be initially free of contamination by explosives is extremely important. It was only after mines were placed at the site that both MECHEM and Nomadics noted positive responses consistent with contamination by explosives.

Detail of the process of test field selection was reported in the MECHEM Progress Report No 1: Site Selection and Establishment dated 27 September 2001 (See Ref 2.5).

5.3 Establishment of theTest Field

Following the finalization of the test field design and the choice of the Rakovo Polje site, CROMAC proceeded to prepare the ground and to establish the test field in accordance with its sub-contract with MECHEM. The entire area was fenced, and the area reduction area was clearly marked by wooden stakes that defined the sampling lanes. The proximity area was marked by staking the corners of the test area around each of the 12 mines in the test area, and a stake was placed in the center of each mined area to mark the position of the mine. Small stones were placed on the ground to mark the 3, 7, and 11-meter radii around each mine. Prof Knapp and Dr Denis Reidy from NVESD completed most of the work on 9 September 2001 when the last mines were laid.

Detail regarding the establishment of the test site was reported in the MECHEM Progress Report No 1: Site Selection and Establishment dated 27 September 2001 (See Ref 2.5).

6 PHASE 1: FIELD SAMPLINGS AND TEST RESULTS

6.1 SAMPLING PROTOCOL

Prior to collecting samples, the flow rate of the MECHEM sampling pumps was adjusted to give a flow rate of 1 liter per second through the filters. The sampling head accommodates sampling onto two filters at once, so for each sample position a MECHEM and a Nomadics filter were loaded into the sampling head. This enabled simultaneous sampling from a given test area onto a MECHEM and a Nomadics filter. It was assumed that the filters sampled exactly the same areas, which further implies that the samples collected are identical in composition. Once installed in the sampling head, the filters are approximately 12 centimeters apart, and depending on how the sampling head is oriented with respect to the ground, the filters may or may not be the same height from the ground during sampling. Hence, there is a chance that the samples were not identical in all cases. Nevertheless, it was assumed that the differences were negligible and that the MECHEM and Nomadics samples from a given test area were identical.

When filters were installed and removed from the sampling head, great care was taken to prevent touching the filters. With some practice it is possible to insert the filter into the sampling head and remove it without touching anything except the filter storage container. This was necessary to help prevent sample cross-contamination. MECHEM filters were marked with a pre-printed label with a unique identifying number. Nomadics filters were labeled by hand in the field with the same number as the MECHEM filter with which it was paired. Although care was taken to prevent errors in recording sample information, some errors did occur. Finally, when filters were transferred back to their respective storage containers after sampling, care was taken to insure that the Nomadics filter was placed in the Nomadics sample storage container while the MECHEM filter was returned to the MECHEM storage container.

In order to collect a sample, the pump operator held the sampling wand so that the filters come into close proximity with the ground, and may occasionally touch the ground. The wand is slowly swept from side to side, keeping the filters close to the ground at all times. The operator walks slowly forward while maintaining the sweeping motion of the sampling wand, attempting to sample as much of the lane as is realistically possible. Multiple pump operators were used during sampling. Although an effort was made to ensure sampling consistency between pump operators, as well as consistency from sample to sample for a given operator, some variability in sampling motion and speed were inevitable.

When sampling lanes, the operator walked approximately down the center of the lane, sampling 2 meters to each side of the centerline. The approximate time required to collect a sample was between four and five minutes per 4 by 50 meter area (this however increased to almost 10 minutes when the vegetation was very dense during the July 2002 sampling). When sampling the circles in the proximity area, the operator walked along each line, sampling two meters to each side of the circle radius. Three sets of samples were collected at each radius. Because the larger radii produced a longer sampling path, samples collected at the larger radii took longer to complete than samples collected at smaller radii. This factor was overlooked during earlier samplings, but was corrected by sampling for the same amount of time regardless of the sampling radius.

6.2 SAMPLING 1: 3 DAYS AFTER MINES WERE LAID (10-13 SEP 01)

This sampling took place three days after the mines were laid and was not a contractual obligation, but was done at the contractors’ own expense. The vegetation was freshly cut and therefore very low, the only exception being the plough furrows that could not be cut low. Weather conditions during the sampling were generally warm and dry, although it had been raining a few days before the sampling. The soil was thus slightly moist, but not wet (see Appendix C for detail weather).

It should be noted that sampling done by both MECHEM and NOMADICS using their respective systems had determined independently that no explosive traces could be detected prior to the establishment of the test site.

During this sampling both the area reduction and proximity areas were sampled, a total of 952 samples (476 each NOMADICS and MECHEM). The standard MECHEM MEDDS filter tube was used by MECHEM; whilst the second iteration PVC NOMADICS filter tube (see Par 8 and Ref 2.21) was used by NOMADICS.

During the initial planning of this sampling, it was generally believed that because the mines had been in the ground for such a short period of time, few if any positive samples would be collected. The basis for this belief was that TNT and related compounds interact strongly with the soil, and as a result are transported through the soil slowly, mainly be the movement of soil water (refer to the work of Phelan summarized in Section 9). Because the time between burial of the mines and sampling was so short, and because the soil conditions were dry, the opinion was that an insufficient amount of time would have elapsed to enable transport of the important landmine chemical signature compounds to the surface of the ground where they could be sampled and detected. However after analysis in Pretoria and Stillwater respectively a surprisingly high number of positive hits were registered.

During the analysis MECHEM, on a suggestion from the client, adapted the usual qualitative (yes/no answer) reporting to a more quantitative analysis based on the number of dogs that indicated samples were positive, and the ease with which the dog indicated the sample. If the dog indicated the sample was positive by sitting as it was trained, more emphasis was placed on the result than if the dog simply showed heightened interest in the sample. The Nomadics samples were analyzed by placing them in front of the inlet of the sensor, which then drew vapors released from the sample into the sensor for analysis. The data was stored electronically, which enabled post-analysis of the data.

Once all data was collected, a committee of three analysts independently (i.e., without knowledge of the other panel member's classification of the sample) scored each sample as positive or negative. If all three analysts scored the sample as positive, the sample was recorded as a positive. If two of the three analysts scored the sample as positive, the sample was labeled as suspect. If only one analyst recorded the sample as a positive, the sample was regarded as negative. Because the sensor also provides a quantitative assessment of the concentration of target compounds in the sample, the strength of the response (recorded as a % reduction in polymer emission intensity after sample introduction) was also logged for samples scored as positive or suspect. These "% quench" values were later used to rank the positive and suspect responses from highest to lowest, with the higher % quench values being given the most confidence.

<u>Deductions</u>. The following deductions can be made from this first sampling:

- The meeting was told that the mines had been in military storage and had been delivered to the site by a truck. The mines were buried pursuant to a plan and laid in the center of designated 4 by 4 meter blocks three days prior to the sampling (Attached ground truth plan, Appendix D). Four types of mines were utilized, and a total of twelve mines were buried at different depths ranging from 10 to 20 centimeters from the top of the mine. The work of Phelan, Jenkins, and others points out that new (unburied) mines that have been stored for a time tend to have high levels of contamination by explosives on their outer surfaces. The high concentration of contamination on the outer surface of the mine could have been rapidly released into the soil. Phelan also suggests that this source of contamination will likely be depleted (released into the soil) rapidly once the mine is placed into the soil. Once the initial surface contamination of the mine is depleted, the mine is still a potential source of contamination, but by a different mechanism. Once the initial surface contamination is depleted, permeation of explosives vapor through the casing of the mine and into the soil becomes the primary route for contamination of the soil. Flux of explosives through the mine casing through structural materials (plastic, rubber, etc.) and through seams or other structural defects in the mine casing is normally expected to be a much slower process than the initial release of explosives due to heavy surface contamination of the mine. Hence, freshly laid mines, with their likely high concentration of surface contamination by explosives, could result in a rapid release of explosive into the soil for a short time (possibly for days or a few weeks) after burial. After this initial "surge" of contamination, the rate of release of contamination into the soil would likely be reduced to a lower, but more constant value that could be sustained for long periods of time (decades). Hence, the initial surge in TNT concentration could be responsible for the high number of positive responses immediately after burial of the mines.

- Another possible explanation for the unexpected detection of the mines was that the minefield could have been contaminated during burial of the mines. For example, if a worker's hands (or shoes) were contaminated with explosives by handling mines, and the worker inadvertently touched the ground with a contaminated hand, or walked across the field with contaminated shoes, the area could also have become contaminated. While extreme caution was taken to prevent this type of contamination, the possibility of contamination via these methods cannot be ruled out.

- Another possibility for detection of contamination immediately after burial of the mines is that the landmine chemical signature could be transported through disturbed soil more rapidly than through undisturbed soil. The observation was also made that a large number of rodents were present in the test field at the time of mine burial and sampling. These rodents burrow in the soil, which leads to disturbance of the soil and possible spread of contamination.

- As previously described, the site was divided into an area reduction test area where sampling was done blindly. The exact locations of the buried landmines were not disclosed until after the results of the final sampling had been submitted to NVESD. In the proximity area where the locations of the mines were known, sampling was done along the 3, 7, and 11-meter radii from the mine center. The purpose was to determine whether and how traces of explosive vapor were spread from the land mine. Testing in the area reduction area was to determine whether and to what extent traces of explosives vapor could be detected. The tests were not designed to locate the exact position of the mines, as neither system is designed as a location detector.

- After three days both MEDDS and Fido detected explosive vapor in the area reduction area and in the proximity area. (See Sampling report and graphical statistical report Ref 2.6 and Appendix E). The correlation between the positions of positive responses by MEDDS and Fido was poor. Reasons for the lack of correlation between the MEDDS and Fido results was likely due to a combination of factors, so no definitive conclusion on a single reason for the lack of correlation was possible. Factors such as accidental contamination of samples during collection, shipping or analysis could have accounted for some lack in correlation, but because care was taken in handling the samples this is probably unlikely. Again, the assumption is being made that the samples are identical. If they are not, this could definitely lead to poor correlation in the results.

- Perhaps the strongest explanation for the lack in correlation between the MECHEM and Nomadics results has to do with what the dog and Fido were actually sensing. The dogs are trained to detect TNT, but may also detect other chemical vapors present in the TNT. Fido detects TNT and a suite of nitroaromatic compounds found in TNT, and also a number of degradation products of TNT commonly found in the soil near landmines. Dogs possibly also rely on the same compounds to detect the presence of explosives, but it is not known whether it is in the same combinations. If the dogs and the sensor are not detecting the same chemical, this could account for the differences in positions of positive responses. For example, the work of Jenkins and others has shown that TNT degradation products may be more prevalent in some areas near a mine, while only a few centimeters away TNT or 2,4-DNT (a contaminant in TNT as a result of the TNT manufacturing process) may be the most prevalent. Hence, some samples may have contained TNT, while others may have contained primarily a TNT degradation product such as 2-amino-4,6-dinitrotoluene. It is possible that Fido detects certain landmine signature compounds that dogs are not trained to detect. It is not that the dogs cannot detect these vapors, but rather that they are not trained to detect them, and hence ignore these vapors. This is an area that should be researched.

6.3 SAMPLING 2: 60 DAYS AFTER MINES WERE LAID (6-10 NOV 01)

This was the first contractual field sampling and took place approximately 60 days after the mines had been laid. The vegetation had started to grow, but was still fairly short and presented no problems. The weather was very poor with rain, low temperatures even snow and high winds of up to 25 knots. During the entire sampling period there was no sunshine (see Appendix C for detail weather). There was significant rainfall between the first and 60 day sampling, and as a consequence the area had been wet for approximately two months.

During this sampling both the area reduction and proximity areas were sampled, a total of 952 samples (476 each NOMADICS and MECHEM). The standard MECHEM MEDDS filter tube was used by MECHEM, whilst the third iteration aluminum NOMADICS filter tube (see Par 8 and Ref 2.12) was used by NOMADICS. Due to the wet weather a large number of sampled filter tubes contained excessive moisture and had developed mould before the dogs and Fido could analyze them. The moulded filters had an extremely offensive odor, and Fido responded to these filters in an atypical fashion that could be easily differentiated from a TNT response. However, the sensor response to mould could have masked responses to samples containing low levels of TNT, and as such presented a problem.

Operationally, this problem can be avoided by not sampling when conditions are wet, by implementing proper storage of the samples, or by analyzing the samples prior to mould formation. It took approximately two weeks from the time the samples were shipped until arrival at Nomadics for analysis. The time required for the samples to reach South Africa was similar. It is not known how the mould affected the dogs.

The results for NOMADICS showed fewer positives than the first sampling whilst the results for MECHEM showed a slight increase in positives. This was in an area that had been constantly wet for approximately two months in an area of sparse vegetation.

Nomadics samples were analyzed based on the magnitude of sensor response rather than by a committee of analysts. Analysis by a panel of analysts was abandoned after the first sampling. This was made possible because of progress made in reproducible sample presentation to the sensor, and a better understanding of how to interpret the sensor responses. A crude computer algorithm was also developed to calculate the sensor response (% quench) for each sample. The responses were then rank ordered, and the samples were classified as positive or negative based on the intensity of response. Responses were generally small, which may have been an indication of the low levels of signature present at the time of sampling. Positive responses were classified as moderate, weak, or very weak based on response intensity.

Thresholds for classifying sample intensity were generally established as follows. First, the average response and sample set standard deviation was calculated for all positive samples. Samples were classified as moderate if they were larger than the average response plus one standard deviation. Weak samples were those that had a response greater than average, but smaller than average plus one standard deviation. Very weak samples were those with a response less than average. Prior to this contract, the Fido sensor had never been utilized for analysis of MEDDS-type samples, so there was no real precedent as to how the results should be interpreted. Hence, development of sample analysis methods was required, and was an effort that was ongoing throughout the contract.

Deductions. Very few deductions can be made from this second sampling:

- It should be noted that the MEDDS and Fido systems again detected explosive vapor at the site. As in the first sampling there was no discernable pattern, nor was there any discernable correlation between the MEDDS and Fido sampling results. The results were random. There was also no correlation between these and the previous sampling results.

- The meeting concluded that the wet, cold and windy conditions were not conducive to effective sampling and had a definitive effect on the results of the sampling. It is known that the vapor pressure of TNT is very sensitive to temperature. Hence, the cold conditions would lower the concentration of explosive vapor in the air, making it more difficult to detect the mines. In addition, the windy conditions would tend to disperse the explosive traces randomly and widely, diluting the vapor to such minute quantities that detection became difficult. The positive traces tended to be more in the middle of the site than at the ends.

- The work of Phelan and others has shown that the movement of water through the soil is the primary means of transport of TNT through the soil. Precipitation tends to transport the chemical signature deeper into the soil, while evaporation of water from the soil tends to bring the signature to the surface of the ground. Because several precipitation / drying cycles had occurred during the two months prior to the sampling, a spread in the contamination of explosives would be expected. This is exactly what was observed, as the number of positive samples increased relative to the previous sampling.

- Regarding the proximity area, the analysis tended to favor the smaller (3 meter radius) circle. The 7-meter radius circle had fewer positives than the 11-meter radius circle. The number of positive samples registered by MECHEM was 31, while Nomadics recorded 32 positive/suspect samples.

- There was again no apparent correlation between the MECHEM and Nomadics results. It was theorized that this might again be due to the dogs and Fido detecting different substances in the filters. However, there is no confirmatory scientific support for that view.

6.4 SAMPLING 3: 9 MONTHS AFTER MINES WERE LAID (15-19 JUL 02)

This sampling was contractually scheduled for March 2002, approximately six months after the mines had been laid. However the heavy rains in Croatia caused this sampling to be postponed twice and finally it took place early in July 2002, approximately nine months after the mines had been laid. Despite the earlier rain the sampling took place in warm to hot sunshine weather conditions with the test field completely dry (see Appendix C for detail weather). The heavy rains had caused prolific plant growth and the vegetation was standing at between 4 and 6 foot high throughout the test field, making manual sampling extremely difficult.

During this sampling both the area reduction and proximity areas were sampled, whilst some grass that Prof Knapp had cut from around mine number 12 in the proximity area was also sampled by MECHEM, a total of 964 samples (476 NOMADICS and 488 MECHEM). The standard MECHEM MEDDS filter tube was used by MECHEM, whilst the fourth iteration aluminum NOMADICS filter tube with the crimped ends (see Par 8 and Ref 2.21) was used by NOMADICS. These tubes worked well, but the flat ends tended to clog with loose vegetation. This could have affected the flow of air through some of the Nomadics samples, and could have influenced the results obtained.

Both Nomadics and MECHEM recorded a very high number of positives. In fact, it was quantitatively the highest number of positives recorded by MECHEM (a total of 175 positive / suspect samples) during any of the samplings. Nomadics recorded a total of 184 positive / suspect samples, which was the second largest number recorded by

Nomadics for all the samplings. Even on the grass that was cut from around proximity mine 12 and placed in an uncontaminated area, MECHEM found that 11 out of 12 samples tested positive. There was also a very clearly discernible "hot spot" of positives in the area where water accumulated during the rainy season (the south-western part of the test field) in both the MECHEM and Nomadics results.

Deductions. The following deductions can be made from this third sampling:

- It should be noted that the MEDDS and Fido systems again detected explosive vapor at the site. As in the first two samplings there was no discernable pattern, nor were there any discernable correlations between the MEDDS and Fido sampling results. The exception to this is that both MECHEM and Nomadics recorded a high number of positives in the area reduction field in the area where water stood as a result of heavy rains in the spring.

- The postponed sampling took place many months later because of the heavy rain in prior months. During the interim period, Nomadics had developed a new tube design. Because of lost freight by an airline, some of the tubes arrived late. This forced the sampling to be completed using one type of tube on the horizontal lanes, and the previous tube type on the vertical lanes. While the tubes were similar, the new tube had rolled ends, while the old tube had crimped ends. This should have had little effect on the performance of the tubes, except for the fact that the tubes with rolled ends were more robust than the tubes with crimped ends. Both tubes were filled with glass beads coated with the same proprietary polymer formulation, but the new filter used beads that were cleaned prior to polymer coating using a different cleaning solution than was used in all other tests. Again, it would be expected that this change would have minimal impact on filter performance.

- Since TNT is soluble in water, TNT could have dissolved in the standing water that accumulated on parts of the site. In addition, water would run down the plow furrows that ran the length of the test field, which could lead to widespread contamination down the length of the furrows. TNT does degrade in water and in soil over time, but some of the degradation products can persist for longer periods of time. It is theorized that water played a large role in spreading the contamination in areas where water stood on the test field, leading to the large number of positives in areas where water stood. In addition, Fido had more positives in the horizontal direction (which is in the direction the plow furrows and water would run) than in the vertical direction. This was true for all samplings except the first sampling, and was also true for MECHEM on all but the first and second samplings.

- Vegetation seems to play a role in the distribution and presence of explosive traces, but the specific sampling of grass was not repeated. Both MECHEM and Nomadics recorded a large number of positives on proximity mine number 12 prior to removal of vegetation from the vicinity of the mine. After removal of the vegetation MECHEM recorded positives from the piles of vegetation that were removed from the area.

- In the proximity area MEDDS had a large number of positives and a stronger preference for the smaller radius (3 meter) but stronger indications in the middle radius.

- There was also an indication that a dry spell after a very wet period could possibly be conducive for better trace explosive detection. The modeling and experimental work of Phelan suggests that drying of the soil after a rain transports TNT and other mine signature compounds toward the surface of the ground where they could be detected. In some cases, formation of a 'crust' of TNT has been noted over mines when weather conditions (rain followed by a hot, dry period) were favorable for its formation. Transport of chemicals such as pesticides and herbicides (some of which behave similarly to TNT) to the surface of the soil after rain has also been widely noted in the literature.

- Like the other samplings, there was no apparent correlation between the location of positives by MEDDS and Fido. There was also no correlation with any of the previous samplings.

7 PHASE 2: OPERATIONAL MINEFIELD SAMPLING AND CLEARANCE

At the initial signing of the contract there was an optional Phase 2 that was intended to continue if Phase 1 of the contract proved successful. Phase 2 entailed the identification of an actual and known minefield in Croatia that would be sampled using both the MEDDS and Fido systems. The minefield would then be physically demined by CROMAC and the position of all mines and UXO found recorded. A comparison would then be made between the actual positions of the mines and UXO and the vapour signature found by the two systems.

Before the end of Phase 1 it became clear that the optional Phase 2 as initially defined was not a viable option since the field samplings had indicated that there was still a vast amount of knowledge about MEDDS and FIDO that had yet to be gained before the systems could be compared in operational circumstances. It was thus decided to modify Phase 2 to encompass the following:

- Two additional vapour samplings were to be conducted, the one in September 2002 and another one during May 2003.

- A filter tube that was compatible with both MEDDS and Fido had to be designed and ready for testing during May 2003.

- A workshop to obtain insight into the leaching of explosives from landmines had to be scheduled. Mr James Phelan from SANDIA Laboratories, an expert on this subject, was invited to present the current state of knowledge on this subject.

- A consolidated final report had to be drawn up and delivered by 31 August 2003.

This revised Phase 2 was approved and the contract signed on 22 Sep 02 (See Ref 2.14).

8 REVISED PHASE 2: TWO FURTHER FIELD SAMPLINGS AND TEST RESULTS

8.1 SAMPLING 4: 18 MONTHS AFTER MINES WERE LAID (31 MAR-5 APR 03)

This was the first sampling under Phase 2 of the contract and was contractually scheduled to take place in September 2002. Unfortunately heavy rains and the approaching winter once again forced this sampling to take place in the Croatian spring.

The harsh winter with heavy snow had completely flattened or destroyed the lush vegetation experienced during the previous sampling. The weather was generally warm and dry, but light rains and strong winds, especially in the afternoons, did hamper the sampling process slightly (see Appendix C for weather detail).

During this sampling both the area reduction and proximity areas were sampled, whilst some specified areas and a quadrant proximity test around mine number 12 in the proximity area were added, a total of 1 120 samples (560 each Nomadics and MECHEM). The standard MECHEM MEDDS filter tube was used by MECHEM, whilst the fifth iteration aluminum Nomadics filter tube with the “Mexican hat” to prevent clogging (see Par 9 and Ref 2.21) was used by Nomadics and MECHEM as the compatible filter tube. These tubes worked well and the “Mexican hat” effectively solved the clogging problem.

For the first time both the Nomadics and MECHEM analysis was done at the MECHEM facilities in Pretoria. The Nomadics filter tubes were firstly analyzed by the MEDDS dogs and thereafter analyzed by FIDO. This was done because Nomadics began heating the tubes slightly before analysis to enhance the vapor signature of the filter. Since it was not known how heating the Nomadics filter affected analysis of the tubes by the dogs, the dogs analyzed the Nomadics (i.e., compatible) filters first, prior to heating and analysis of the tubes by Nomadics.

Heating of the tubes was first suggested by personnel in the MECHEM canine facility, who as a matter of practice also heated the Nomadics (aluminum casing) filters slightly when the dogs were having difficulty detecting known positives because of cold conditions during analysis. Using MEDDS dogs that had been “re-trained” on the Nomadics filter tubes, a surprisingly high number of positive indications were found. An administrative problem was encountered in that a number of filter tubes were placed in the wrong containers (outer vials) during sampling causing contamination of the

Nomadics tubes by the plasticizer left behind by the MEDDS tube in the container. This mistake made it impossible to detect the presence of TNT on the plasticizer-contaminated filters using Fido.

<u>Deductions</u>. The following deductions can be made from this fourth sampling:

- It should be noted again that the MEDDS and Fido systems both detected explosive vapor at the site. As in the first two samplings there was no discernable pattern, nor was there any discernable correlation between the MEDDS and Fido sampling results. The results were random. There was also no correlation between these results and any previous sampling results.

- Nomadics recorded the largest number of positives for any sampling, and the average response to positives was the largest of any sampling. However, MECHEM recorded the fewest positives for all samplings except the first. The reason for this difference is unknown.

- According to the work of Phelan and Jenkins, the cold winter should have significantly reduced degradation of TNT, while the wet conditions would favor degradation as well as the transport of TNT to the surface of the ground when the soil dried. There was thus the anomaly that whilst the cold winter conditions would inhibit degradation, the moisture on the other hand would be conducive for degradation. It is presently an open question as to which of these factors would have played the stronger role in either inhibiting or encouraging degradation. This requires further study into the results of climatic conditions on the degradation of TNT. Once the soil temperatures warmed during the spring and summer, the buildup of TNT in the soil would begin to degrade by the action of microbes in the soil. The breakdown products of TNT by this process are amino-DNTs, which Fido can detect. It is not known if dogs rely on this substance to detect mines. This could account for the higher number of positives by Fido.

- Regarding the filter tube it was noted that this was the first time that an analysis was done using a common tube. From the results it is apparent that the dogs registered more positive indications on the MEDDS tube, but a statistical analysis on the results performed by Nomadics suggests that the positives registered on the Nomadics tubes were on average closer to mines than positives registered on the MEDDS tube.

- As with previous tests the meeting noted that there was no correlation between positions of positive indications, which may again suggest that the MEDDS dogs were not analyzing the same substance as Fido. There was, however, insufficient scientific proof to confirm these suspicions.

- The “Mexican hat” had solved the problem of clogging up in the Nomadics filter tube.

- Administration of the systems, especially where more than one type of filter tube is used, is very important for the success thereof.

8.2 SAMPLING 5: 20 MONTHS AFTER MINES WERE LAID (26-30 MAY 03)

This was the final sampling under the contract and due to unforeseen circumstances had to be done within 7 weeks of the previous sampling. The weather was generally warm and no rain had fallen since the previous sampling. During the sampling very light drizzle occurred but it had no real influence on the sampling process (see Appendix D for weather detail). Due to the absence of rain the vegetation had not grown much and was at about ankle to knee height.

During this sampling both the area reduction and proximity areas were sampled, whilst the same specified areas and quadrant proximity test around mine number 12 in the proximity area were again performed, a total of 1 120 samples (560 each NOMADICS and MECHEM). The standard MECHEM MEDDS filter tube was used by MECHEM, whilst the same NOMADICS filter tube with the "Mexican hat" as used in the forth sampling was used by NOMADICS and MECHEM as the compatible filter tube.

The same method of analysis in Pretoria was used as previously with NOMADICS improving their analysis process substantially so as to be able to deliver analysis results in a much shorter space of time. Using a different coloured sticker to distinguish the different filter tubes from each other, the human errors experienced in the previous sampling were greatly reduced.

Deductions. The following deductions can be made from this fifth sampling:

- It should be noted again that the MEDDS and FIDO systems again detected explosive vapor at the site. As in the first two samplings there was no discernable pattern, nor was there any discernable correlation between the MEDDS and FIDO sampling results. The results were random. Once again no correlation could be found between these results and any of the previous sampling results.

- As in the April 2003 sampling, the MEDDS dogs recorded more positives on the MECHEM filter than the Nomadics filter.

- The meeting noted that in the area reduction area the number of MEDDS and FIDO positives had decreased, although there were more positive indications for FIDO than MEDDS. In the proximity area, the number of positive indications was roughly the same, but the number of MEDDS positives using the NOMADICS tube was exceptionally high.

- Human and administrative mistakes can be easily rectified as was proven by placing colored stickers on the outer vials and having two persons checking each filter tube.

9 REVISED PHASE 2: WORKSHOP ON THE LEACHING OF EXPLOSIVES FROM LANDMINES

9.1 INTRODUCTION

During Phase I of the project, it was determined that the various factors that influence the spread of explosive signature were not fully understood by all parties involved. To help rectify this, in October 2002 the team hosted a workshop on the fate and transport of explosives in the soils in the vicinity of a landmine. The workshop, conducted by recognized authority James Phelan of Sandia National Laboratories, was widely regarded as a resounding success by the dozen or so individuals from MECHEM, NOMADICS, CSIR, and NVESD in attendance. In retrospect, it may have been better to have the meeting at the beginning of the contract.

The course curriculum was based on Sandia Report SAND2002-0909 entitled “Chemical Sensing for Buried Landmines-Fundamental Processes Influencing Trace Chemical Detection” and was distributed to all workshop attendees. Project Report 10 provides details on the topics discussed at the workshop. The Sandia report is included as an attachment to this document.

9.2 FATE AND TRANSPORT ISSUES

Space does not permit a detailed review of the subject matter. However, the following paragraphs summarize some of the key subject matter described at the workshop.

Figure 1 illustrates some of the processes that occur in the soil near a buried landmine. Vapors of signature compounds escaping from the mine are quickly adsorbed onto soil solids or dissolve in soil water. Molecules of explosives such as TNT are strongly adsorbed by most surfaces. Due to the large surface area presented by soil particles and because of the adsorptive properties of explosives to solid surfaces, the majority of the explosive-related compounds (ERCs) partition onto the soil particles immediately surrounding the buried mine. The partitioning of ERC into liquid and gas phases is governed by partition coefficients that are primarily a function of soil moisture content, and secondarily a function of temperature and soil type. For a typical soil, approximately 95% of the total mass of ERC is adsorbed onto soil solids, followed by approximately 5% into soil water, with a trace (approximately 1×10^{-6} %) partitioning into the vapor phase. ERC accessibility and accumulation are further limited by irreversible binding to soil solids and by processes such as microbial degradation. The half-life of TNT in certain soils when the conditions for microbial degradation are favorable is short, on the order of a few days, while 2,4-DNT is much more stable in the environment.

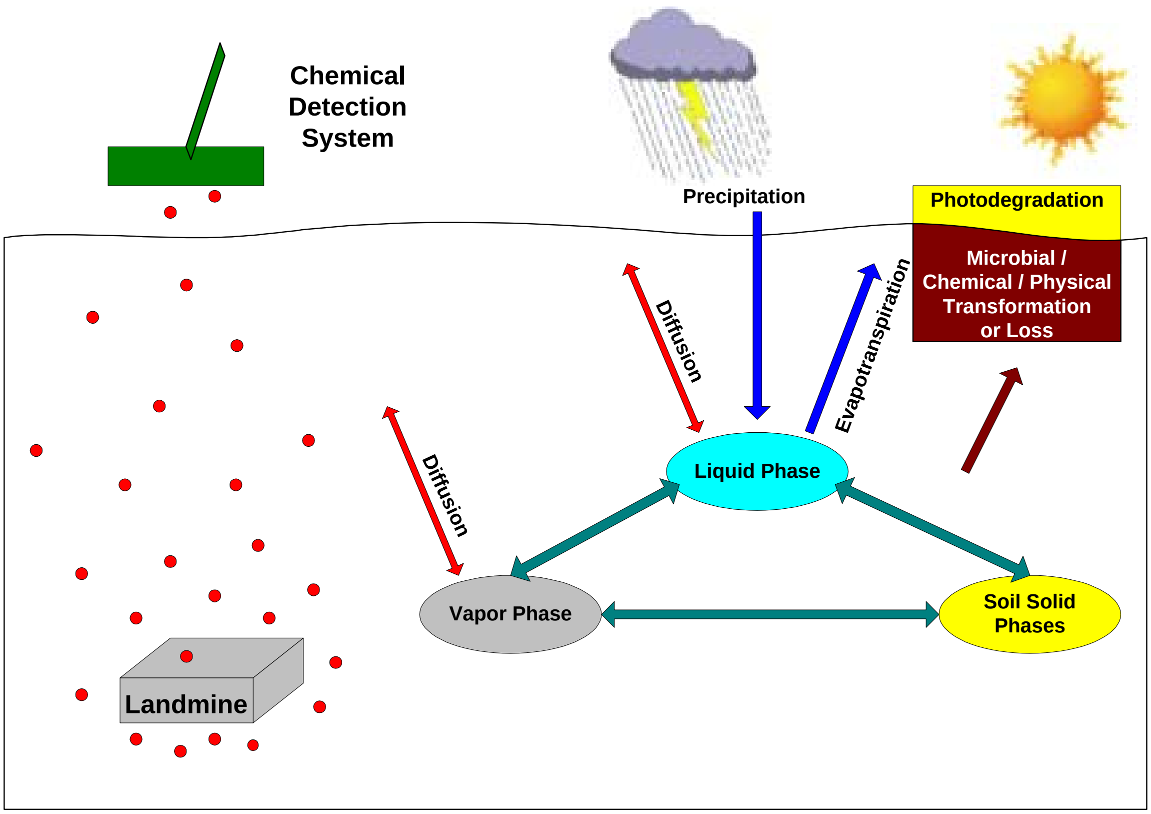

Figure 1. Processes affecting the fate and transport of landmine signature compounds in soil.

The primary mode of transport of ERC to the soil surface is through the movement of water in the soil, not by molecular diffusion. Precipitation tends to draw ERC downward through the soil. Conversely, water evaporating from the surface of the ground brings contaminated subsurface water to the surface (evapo-transpiration). As the water evaporates, it deposits the semi-volatile signature compounds preferentially on the comparatively drier soil particles at the surface of the ground. This behavior has also been observed for the transport of low-volatility pesticides whose chemical properties are similar to explosives. Molecules of signature compounds then escape from contaminated soil particles at the surface of the ground and into the boundary layer of air near the surface of the ground. The concentration of ERC in the boundary layer of air depends on the solid to vapor partition coefficient that is, as previously described, a function of soil moisture content, temperature, and soil type.

Photochemical degradation of some analytes may occur in soil exposed to sunlight. Some of these products such as 1,3,5-TNB are more volatile than the parent compound, and escape from the soil more readily. These more transient compounds may not offer the consistent signature needed for reliable vapor detection. Analysis of numerous surface soil samples from the Fort Leonard Wood minefield has revealed the presence of 20 different ERCs in the soil near mines.

The following items were discussed in detail during the workshop:

9.3 NUMBERS IN CHEMISTRY

This discussion was held to ensure that all attendees understood the standard terminology used to describe and compare the quantities of material of trace chemical landmine detection.

9.4 TARGET CHEMICAL COMPOUNDS

It was highlighted that 100% pure TNT does not exist in practice. Whilst the solid state of TNT is mainly made up of 2,4,6-TNT, the vapor state also has high concentrations of 2,4-DNT and 1,3-DNB present. It is not known if mine detection dogs respond to the TNT odor, or rather to DNT or DNB or a combination thereof.

9.5 LANDMINE CHEMICAL EMISSIONS

The amount of explosive leakage, or *flux*, from a landmine varies depending upon:

- Permeability of the casing material used (metal, hard plastic, soft plastic)
- Presence of holes, fuse wells, cracks, and other openings
- Temperature (i.e., there is greater flux at higher temperatures)
- Amount of soil moisture, and standing or flowing water (flux is greater into water than into air and soil)
- Painting on mines limits permeability

9.6 CHEMICAL DISTRIBUTION IN SOILS

Soil is a complex medium containing air, water, and soil particles. The transfer of explosives through soil is dependent upon moisture content, physical makeup (e.g., amount of sand, loam, and clay), as well as organic material content.

9.7 CHEMICAL DEGRADATION IN SOILS

Degradation is of critical importance for the determination of the amount of chemical available as cues for trace chemical detection, since it offsets the gain from landmine chemical emissions. Degradation rates depend upon moisture content, microbial reactions, physical makeup, organic content, temperature, and physical breakdown reactions. Note that degradation by-products may be valuable vapor cues for dogs. Especially the presence of aminos as by-products of both TNT and DNT warrant further research.

9.8 CHEMICAL TRANSPORT IN SOILS

This was an important discussion since TNT odors are often detected some distance away from buried landmines, especially in areas with substantial water run off. Landmine signature chemical transport in soil is crucial to understanding the amount of vapor available as a cue to the sensor (dog or machine). The chemical must be transported from the proximity of the landmine to the ground surface to become available as a cue. In most cases vapor and solutes move through soils using two principal processes, namely diffusion and convection. Diffusion is motion driven by differences in concentration (high to low) between locations and occurs with both vapors in air and solutes in water. Convection on the other hand is the act of transporting chemicals in a stream of air or water. During rainfall solutes in water are convected downward, while evaporation convects solutes upwards. The movement of air in soils induced by wind and barometric pressure can also convect vapors downwards into and upward out of surface soils.

9.9 WEATHER FACTORS AFFECTING CHEMICAL SENSING

Weather factors that affect chemical sensing include atmospheric pressure, atmospheric temperature, atmospheric relative humidity, solar radiation (short wave), long wave radiation, wind velocity, precipitation and plants. In order to determine the best and worst times for chemical detection, the influence of weather conditions on the boundary layer must be understood.

9.10 LANDMINE-SOIL-WEATHER SYSTEMS ANALYSIS

This discussion focused on a computer simulation model, T2TNT, which is currently under development to try and combine all the various properties and processes affecting the chemical signature from buried landmines. In summary it can be stated that this tool can be used to evaluate various scenarios; certain combinations of particular mine types, soil properties, and weather patterns. Differences in soil vapor emissions for scenarios in regional context (Croatia, Afghanistan, Cambodia, Mozambique, Angola, etc) may demonstrate the critical nature of maintaining mine detection dog (MDD) performance or the futility of certain situations where vapor levels are well below typical MDD vapor sensing capabilities.

9.11 ANALYSIS OF SOILS FROM THE VICINITY OF LANDMINES

The sampling and chemical analysis of soils and vapor above the soils provide direct evidence of the type and magnitude of landmine signature chemicals available as cues for the detection dogs. Soil sample results have found TNT, DNT, 4A-DNT and 2A-DNT (the latter two being degradation by-products of TNT) as the most prevalent landmine signature chemicals. The absence of DNB is rather interesting, whilst the possibility that the dogs actually smell the amino's once again becomes relevant. Once again further research into this field is suggested. Surface soil samples do not always show detectable residues at every sample location.

9.12 VAPOR SENSING THRESHOLD OF DOGS

A very short discussion was held on this topic since very little work has been done that completely describes how dogs can detect and locate hidden objects, vapors, etc. Any research into this field is also made more difficult by the fact that the dog's vapor detecting capability is much lower than laboratory chemical measurement instrumentation and by the dog not being able to give quantitative measurement but only a yes or no answer.

9.13 AREAS OF CONCERN/INTEREST

The workshop participants for further discussion identified seven areas of particular concern. :

1) Spreading of TNT contamination and surface crust forming.
2) The role of vegetation in chemical detection.
3) The role of aminos.
4) Rapid photodegeneration.
5) Mines containing Tetryl and not TNT.
6) The elimination of confounding factors during MEDDS/FIDO Sampling.
7) Molecular movement into the air.

9.14 CONCLUSIONS

The participants at the workshop noted the following:

- The workshop had been very beneficial to the increased understanding of buried landmines and trace chemical detection of those landmines.

- Many of the views expressed by Mr Phelan of Sandia National Laboratories had been confirmed in the comparative testing or there was support for the propositions. In particular TNT degradation, the effect of sunlight and moisture (water), bacterial degradation, vegetation, the leaching rate of different mines are important factors that must be considered.

- Further research is required, particularly in the evaluation of chemical flux from mines into soil. This will be specific to each land mine type. The role of soil moisture content on landmine flux should also be investigated further. The apparent randomness of the distribution of explosive traces near mines is also an area that should be researched further.

- Further scientific work is required to determine the actual chemical substance that is being detected by the MEDDS dogs. The issue of the role of amino-DNTs needs further attention, particularly as it related to detection.

- While much knowledge was gained, many questions remained unanswered. These will require further study and research.

- The workshop was one of the most valuable deliverables of the project.

10 REVISED PHASE 2: COMPATIBLE TUBE DESIGN

10.1 Overview

The primary reason for this object was to produce a sampling tube that would be compatible with both the MEDDS and Fido systems so as to to ensure that the results obtained by the systems would be really comparable. It was believed that true comparitability would only be achieved by analyzing the same tube. Prior to formal award of this contract, initial tests of the Nomadics Fido TNT detector with MEDDS cartridges was undertaken. Dr. Vernon Joynt and Mr. Braam Rossouw of MECHEM delivered both positive and negative MEDDS control samples to Nomadics in Stillwater. Tests using the tubes with a Fido detector were performed, revealing that the existing MEDDS sampling cartridge was incompatible with the Fido detector. Because of this incompatibility, several design iterations of a new tube have been completed by Nomadics. These designs have undergone considerable testing in the laboratory and have received use in field-testing. A tube has been developed that is compatible with the Fido sensor and canines. An attempt was also made to adapt the Fido sensor to improve compatability with the MECHEM MEDDS filter.

During initial discussions during October 2002 it seemed as if it would be possible to make the existing MEDDS and Nomadics tubes compatible with each other's systems. This was then also set as an original goal and to this end MECHEM managed to re-train three of its MEDDS dogs to work with the Nomadics tubes. Due to factors explained in detail further in this section Nomadics were not able to make Fido compatible with the MEDDS tube. This led to the decision to use the Nomadics tube as the compatible tube during the last two field samplings.

10.2 Tube Design Goals

The overall design goal was to develop a sampling tube that is compatible with both the MEDDS system and Fido. Because the MEDDS system is a mature system that has been utilized with good results, an attempt was made to keep modifications to the MEDDS tube design to a minimum. Hence, the emphasis was on identifying the factors that make the present MEDDS tube design incompatible with Fido, and once these factors were identified, to make the changes necessary to enable production of a tube that is compatible with both systems. Hence, the geometry of the tube (i.e., the diameter and length of the tube) was not being changed so that the new tube design will work with the present MECHEM vacuum pump without modifications. In addition, an effort was made to maintain the same backpressure with both the Nomadics and MEDDS tube so that the flow rate is as similar as possible for a given pump speed. The need to keep the cost of tube production low was also a consideration.

10.3 Nomadics Tube Design History

Table 1 is a description of the various iterations of tube designs developed by NOMADICS. The table lists variations between tube iterations and relevant comments relating to use and performance of the tubes. Initial tube designs were quite fragile, many of which did not survive shipping to the site of field tests in Croatia. This problem has been addressed, and the latest design is much more robust. Clogging of the tube during sampling, a problem with earlier designs has been greatly reduced. A tube has now been developed that is compatible with FIDO and the canines, and was used during comparative testing of FIDO and canines in Pretoria, South Africa in February 2003, and was used in the April and May 2003 Croatian field tests.

Design	Use	Comments	Illustration
Mechem tube with gauze	Initial evaluation of compatibility between FIDO and MEDDS (2000)	Cartridges were determined to be unsuitable for use with FIDO due to atypical sensor response likely due to plasticizers in gauze material.	
Mechem tube partially filled with coated glass beads in place of gauze	Site selection sampling (July 01)	FIDO results were comparable to what was determined through use of MEDDS dogs. FIDO had more positive responses. It is not known if this was good or bad since there was no ground truth. It was also difficult to seal the new NOMADICS tube during the manufacturing process, nor could it be heated to improve release of explosive during the analysis process.	
Grey PVC tube partially filled with coated glass beads	Time 0 sampling (Sept 01)	Cartridge was difficult to work with in the field due to tube deformation and also had clogging problems. Cartridges were analyzed with FIDO after being processed using a heating/purging subsystem.	

Crimped metal tube filled with coated glass beads	+45 day sampling (Nov 01)	Tubes were more durable and survived shipping better. Sampled cartridges contained a large amount of water due to poor sampling conditions. This resulted in mold in cartridges which may have affects on analysis due to possible microbial degradation of TNT.	
Improved metal tube filled with coated glass beads	July 02 sampling	At a high level, results appear somewhat comparable to MEDDS.	
Same casing and material with addition of debris shield	April and May 03 samplings	Eliminated clogging problem while maintaining compatibility with MEDDS canines	

Table 1. NOMADICS tube history

10.4 Factors Contributing to Incompatibility of the MEDDS Tube With FIDO

After laboratory testing of the MEDDS tube with FIDO, it was determined that a constituent of the plastic gauze used in the MEDDS tube was the source of incompatibility. Tests were conducted in which MEDDS tubes were disassembled, and the component parts were then analyzed with the FIDO sensor. Table 2 lists the results of these tests. The response of FIDO to each component is noted in the table. The only component that produced a response

Component	Response
Plastic Storage Tube	No Response
Outer PVC Tube	No Response
Inner PVC Component	No Response
PVC Gauze	Positive Response

Table 2. Response of FIDO to MEDDS tube components.

was the PVC gauze used as a filter medium. Upon opening the plastic storage tube, a distinct 'plasticizer' smell can be noted. The exact plasticizer used in the manufacture of the gauze is unknown. Because platsicizers were suspected as the interfering substance, a test was performed to determine whether or not FIDO would respond to plasticizers. Dioctyl phthalate, a common plasticizer, was sampled with FIDO, and a response very similar to that of the MEDDS tube was noted. In both cases, an increase in polymer emission intensity was noted upon sampling, which is not the typical response to TNT. TNT produces a strong reduction in polymer emission intensity. The response to the plasticizer is therefore different than the response to TNT, but the problem lies in the fact that for a sample containing plasticizer and TNT the response of the sensor is a composite of the two responses. Because the responses are opposite in magnitude, it is conceivable that a response to the MEDDS tube could mask a weak response to TNT. It should be noted that FIDO does not respond to most plastics, most of which contain a variety of plasticizers (for example, FIDO did not respond to the other plastic components of the MEDDS tube). Without knowing the exact identity of the plasticizer, or other constitiuents of the gauze, it is difficult to determine what FIDO is sensing in the gauze. The leading candidate is the plasticizer, but this has not been determined conclusively at this time.

Because the vapor pressure of explosives increases rapidly with temperature, heating the tube slightly increases the rate at which explosive desorbs from the tube, increasing the probability of detecting explosives trapped in the tube. However, heating the MEDDS tube also increases the concentration of the interfering compound emanating from the tube, making it even more difficult to use the tubes with FIDO when the tubes are warm.

10.5 Selection of Compatible Tube Materials

Selection of compatible materials used in construction of tubes was given a great deal of consideration. When TNT vapor is trapped in the tube, a number of processes occur that directly affect the detection process. TNT strongly interacts with certain materials. The strength of these interactions ranges from strong to very strong, approaching that of the strength of a chemical bond. TNT interacts strongly with many metals, particularly those that form an oxide coating. TNT adsorption (i.e., binding of TNT on the outer surface of a material) to certain metals can be irreversible. If this occurs, TNT bound in this way will not be detected either by dogs or FIDO because it is trapped on the surface of the cartridge. In order for TNT to be detected, the binding must be at least partially reversible so that some of the material can desorb into the vapor phase for detection. On the other hand, if TNT is too weakly bound inside the tube, it can escape during sampling, which is again detrimental to detection. Hence, a balance between the strength of interaction of TNT with tube materials is crucial to developing a successful tube design.

A different process that can occur in the tubes is absorption. Absorption is the incorporation of a material into the inner structure of another material. Porous materials, including most plastics, can absorb large quantities of materials such as TNT. When TNT is adsorbed onto the outer surface of a porous material, over time the TNT can diffuse into the pore structure of the material, at which point it is no longer considered 'adorbed', but 'absorbed'. Absorbed TNT is often not readily available for detection because of the extremely slow rate at which absorbed TNT diffuses out of the material into which it is absorbed. Under certain conditions we have observed that the rate of diffusion of TNT out of the plastic is slower than the rate of desorption of the TNT from the surface of the plastic. Hence, diffusion of TNT out of porous materials can be the rate limiting process determining the vapor phase concentrations of TNT produced by contaminated porous materials. Over time, a porous plastic such as polyethylene that contains absorbed TNT may liberate TNT into the air, but the process can be slow, and the concentration of TNT in the air near the plastic at any instant in time can be very low. This may make the TNT more difficult to detect. TNT could conceivably diffuse through plastic storage containers and be lost over time, which is another important design consideration. There are methods to increase the rate of desorption of TNT absorbed into materials, including limiting the thickness of the porous material or raising its temperature. Raising the temperature of the material tends to increase the diffusion rate of TNT through the pores of the material, increasing the rate at which TNT escapes from the material. Materials were indentified that bind TNT strongly enough so that it can be efficiently trapped in the tube, but not bound so strongly that it does not desorb into the vapor phase to enable detection of TNT by dogs or FIDO.

The current NOMADICS tube design utilizes an aluminum outer tube packed with borosilicate glass beads. The beads are retained inside the aluminum tube using stainless steel screens. These materials are all non-porous, so all the TNT trapped in the tubes is surface adsorbed. We have attempted to limit use of porous materials that may absorb TNT. This choice was made in an effort to increase the availability (vapor pressure) of TNT in the tube during analysis, which should increase the probability of detection of TNT. Coatings of porous materials on the glass beads that cause them to retain TNT more strongly were also investigated. The more retentive coatings were investigated because of the possibility of TNT breakthrough during long sampling cycles. The more retentive coatings reduce the chances of this occurring.

10.6 Other Work Completed

A persistent problem with the NOMADICS tube design has been clogging of the tube with soil and plant debris during sampling. A solution to this problem was developed. A second screen shaped like a Mexican sombrero was added to the inlet end of the tube. The second screen extends in front of the inlet of the cartridge, much like the gauze extension utilized in the MECHEM design. During field testing conducted in April and May 2003, the new design did not exhibit the tendency to clog, and was much more robust with few cartridge failures.

These new tubes have also been used with the MECHEM MEDDS canines with good results. Laboratory testing of the compatible tube was conducted in South Africa at the MECHEM facility in Pretoria. During these tests, the response of both FIDO and canines to laboratory prepared samples was comparable, demonstrating the compatibility of the new tube design. The new compatible tube design was also used during the April and May 2003 samplings in Croatia. Both FIDO and the canines analyzed the compatible tube. Both FIDO and the dogs noted many positive responses. However, unlike the excellent correlation between FIDO and dogs during the February laboratory comparative testing, the correlation between FIDO and canine response for the Croatian field samples was disappointing. The reasons for this lack in correlation between responses have been difficult to determine.

Compatibility of the FIDO sensor with the MEDDS filter was also an area of investigation. As stated earlier, the plasticizer used in the MEDDS filter causes the fluorescent polymer-sensing element in the FIDO to increase in emission intensity. It is believed that this increase in emission intensity is due to swelling of the polymer that occurs when molecules of plasticizers dissolve into the film. As the concentration of plasticizer in the film increases, eventually a point is reached where the emission intensity reaches a maximum. When the plasticizer concentration in the film reaches this ‘saturation’ point, it was observed that the films do not respond to MEDDS filters. However, films ‘saturated’ with plasticizer exhibited a reduced response to TNT. An attempt was made at reducing the plasticizer concentration slightly from the ‘saturated’ concentration to increase the response to TNT, but when this was done the response to plasticizer, while reduced in magnitude relative to when no plasticizer was added to the film, was significant enough to complicate sample analysis. While progress towards making FIDO compatible with MEDDS filters was made, further work is necessary to achieve this goal.

11. THEORIES AND CONCLUSIONS

11.1 At the final project review meeting, the five samplings were reviewed. There were a number of factors that could influence sampling and the results. These are listed below, in no particular order:

(1) The type of mine.
(2) Activity of rodents in the field.
(3) Water/wind.
(4) Vegetation.
(5) Sensitivity of Fido and the MEDDS dogs and the substances that they detect.
(6) Time of day and other environmental conditions.
(7) Age of minefield.
(8) Sample time per square meter.
(9) Mine depth and condition.
(10) Problems with sampling machines.
(11) Human factors (fatigue, etc).
(12) Degradation of samples during shipping and storage.
(13) Tube temperature.

11.2 Regarding the type of mine, it was noted that the construction of the metal mines used in the test was excellent, and that these mines were very well sealed. This would lead to lower explosive flux rates from these mines compared to less well-constructed mines or plastic mines. It is a known fact that the PROM mine is very difficult to find even with free-running dogs. The TMA mine was well made, but the PMA2 and PMA3 plastic mines were more susceptible to leaching due to the fact that most plastics are relatively permeable to explosives. In addition, plastic can degrade after time, increasing the flux rate of explosives into the soil. While the PMA3 mine sometimes contains tetryl, the dogs and Fido were apparently able to detect these mines. It is not known if the PMA3 mines used in the test are TNT or Tetryl-filled. Dogs can be trained to detect tetryl, and Fido will also respond to tetryl, but the vapor pressure of tetryl is significantly lower than TNT, making it more difficult to detect.

11.3 Mine depth did not seem to play a role. Counter-intuitively, it appears that the deeper mines indicated stronger positives initially.

11.4 It is apparent that water, wind and air have an influence on the detection of mines using vapour detection techniques, but it is still unknown to what extent these factors influence such detection.

11.5 Initial tests suggest that vegetation may be important to vapor detection, but in the absence of sufficient data it is not possible to verify this finding.

11.6 It was acknowledged that there is a perception to treat a dog as a machine. Constant training between the dog and its handler is required to optimize performance. A constant control over the process is required.

11.7 It was noted that Fido had improved dramatically since the start of the contract. A number of improvements to the initial model, improvements in data processing and analysis, and improvements in the method of filter analysis had all improved the performance of Fido.

11.8 Regarding both MEDDS and Fido it was observed that the humidity during the sampling process was not important. This means that sampling time per day need not be restricted as previously believed due to limitations of humidity and air temperature. The availability of dust and particles for sampling were more important as well as moisture in the soil. Temperature and humidity played a more important role in the analysis part of the process. It would seem that the results are better in dry conditions where dust particles are freely available.

11.9 The test site is very young, and the buried mines should be studied for a longer period of time.

11.10 It appeared that the amount of time spent sampling near or over the area of a landmine is important. The more time spent sampling near a mine, the greater the concentration of explosive trace collected in the filter.

11.11 It was observed that the sampling machines were very satisfactory, but that contamination of filters was possible by storing them close or nearby oil or gasoline from the machines. It would appear that the gasoline smell did not influence the dogs' detection abilities, this could however not be proven and should thus be avoided.

11.12 Human factors play an important role in the collection and marking of the filter tubes, and better administrative arrangements including training and supervision reduced errors.

11.13 It was noted that further study was needed on the effects and influence of bacterial and microbial action and degradation. Not enough was known about this subject.

11.14 Although there were not sufficient tests done to scientifically prove it, the dogs did find more positives using the MEDDS tubes than with the Nomadics tubes.

11.15 The results of the proximity testing for the April 2003 sampling were interesting in that the Nomadics analysis found 81 positives: 27 at 3 meters, 26 at 7 meters, and 28 at 11 meters. There were a total of 108 samples. There was no apparent radial preference

11.16 The number of positives in the proximity area for the April 2003 sampling by MEDDS was lower: only 40% of 108 samples were positive. Using the Nomadics tubes, 38% of the 108 samples were positive.

11.17 For the May 2003 proximity sampling, Fido detected 59 positives of 108 samples (55%): 18 at 3 meters, 19 at 7 meters, and 22 at 11 meters. There was again no radial preference.

11.18 MEDDS with MECHEM tubes found 71% of the samples for the May 2003 proximity sampling to be positive, while using the Nomadics tubes 83% of the proximity samples were positive.

11.19 It was again noted that the presence of amino-DNTs in samples could have an important effect. Fido detects amino-DNTs, while it is not known if the MEDDS dogs detect this substance. Further study is required.

12 RECOMMENDATIONS

The following recommendations are made as a consequence of the work completed under this contract:

12.1 The test field was likely too heavily populated with mines in the area reduction part of the test site. This may have led to overlap of the areas of contamination produced by each mine, making it difficult if not impossible to correlate positive responses with a given mine position. It was also not possible to determine how far contamination spreads from a mine from the proximity data because contamination was routinely detected at the largest radius sampled from each mine. In retrospect, these mines should have been buried much more than 30 meters apart. The layout of the area reduction test field did not allow for areas that were verifiably free of contamination. A larger test area is recommended, coupled with a lower mine burial density for the next time such tests are conducted. A different sampling plan is required to determine areas that are free of mines.

12.2 More tests are required on MEDDS and Fido to determine which substances are being detected.

12.3 A complete qualitative and quantitative analysis of soil samples taken from the minefield is required to make a determination of the spread of contamination and its components.

12.4 MEDDS and Fido filters need to be tested on TNT and decayed substances separately.

12.5 Much more information is required regarding the climatic cycle when collecting samples.

12.6 Fido lacks operational experience and conditions and it is recommended that further tests be done in operational circumstances. The tests performed under this contract were the first in which the sensor was used to analyze MEDDS-type samples.

12.7 Especially for tests in which such a large number of samples are collected, positive steps must be taken to reduce or eliminate administrative and human errors through training and education.

12.8 Further sampling could be carried out at the Croatian test site using a different sampling plan. In retrospect the close proximity of the mines to each other makes any further testing using the present sampling regime impractical and ineffective. The only testing that is still possible is to treat the present test field as a minefield and to test for explosive traces in areas outside as well as inside the test field to test the area reduction capability of the two systems.

12.9 Further testing and development is required to collaborate results using a common tube.

12.10 More information needs to be shared on explosive vapour detection to enable it to be completely accepted in the humanitarian demining community as a reliable area reduction method.

12.11 Side-by –side execution of research is paramount to the continuing success of the exercise

12.12 More partners need to be identified that can benefit from the technology, particularly in the NGO demining community.

13 SUMMARY

Finally the meeting examined the scope of the contract and noted that five comparative test samplings had taken place in Croatia at the designated test site. In every sampling both MEDDS and Fido detected the presence of explosive vapour. This pointed towards the ability of both systems to detect the presence of trace explosives in an area containing landmines. In retrospect the test field layout did not allow for the clear identification of areas free of landmines with any amount of certainty. Taking into consideration that both MEDDS and Fido have been designed as area reduction systems rather than mine detection systems, the focus should have been on such areas clear of landmines. It is recommended that a more effective test/test field be used to remedy this situation in future to determine areas free of landmines with a greater degree of certainty. Even though not part of the statement of work, this contract contributed greatly in making both MEDDS and Fido more effective in this area reduction role.